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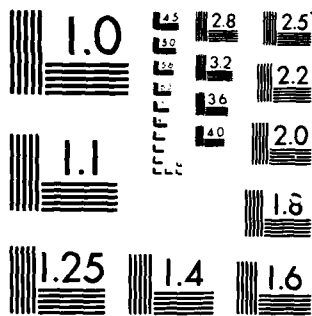
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Properties of Organic Superconductors

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Abstract:

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This is the final report of our three-year study of the properties of organic superconductors. We will only summarize the results of the last years' work (September 1982 through September 1983) since our previous reports covered the initial two years. The details of our work can be found in the reprints accompanying this report.

Our major results were the following:

- 1. Discovery of a new class of organic superconductors based on the (BEDT-TTF) molecule. This discovery has proven to be very important since recent chemical modification of our (BEDT-TTF) compound has led to a superconducting transition temperature of 8K, quite high for an organic solid. This offers the possibility that superconductivity can be found at temperatures greater than inorganic materials. However, this will require better understanding of the present organic materials and synthesis of new materials. Our characterization of the (BEDT-TTF)₂X superconductors included transport, magnetic and structural properties and these are discussed in the references.
2. Measurement of the far IR properties of (TMTSF)₂ClO₄. These results proved that a large superconductivity gap does not exist in (TMTSF)₂ClO₄, contrary to previous speculations and erroneous interpretation of data by other workers. This rules out the possibility of superconducting fluctuations in the (TMTSF)₂X class of organic superconductors. Our results do show, however, that the far IR spectrum of these materials is anomalous when compared to an ordinary metal. This suggests that some type of collective mode may be present in (TMTSF)₂ClO₄ but it will require more work to determine the exact nature of this collective mode and its effect on the physical properties.
3. Observation of new features of the magnetic-field-induced transition in (TMTSF)₂ClO₄. The field-induced transition (FIT) was first observed by us in the PF₆ salt and was discussed in our prior reports. This transition is quite anomalous and appears to be unique in solid state physics. In an attempt to better understand the FIT, we measured the Hall effect and the magnetoresistance of (TMTSF)₂ClO₄ as a function of magnetic field up to 20T at the MIT National Magnet Laboratory. Our results show that there is, in fact, a series of transitions with increasing field and the number of carriers is decreased at each transition. Moreover, the Hall effect is similar to that found in the Quantum Hall effect. It seems clear that our work will have a significant impact in the future understanding of this novel transition.

In summary, our basic research during the past three years of ONR partial support has led to a number of fundamental new discoveries and a better understanding of the physics and chemistry of organic superconductors.

Availability Codes	
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Tetramethyltetraselenafulvalenium Perchlorate, (TMTSF)₂ClO₄, in High Magnetic Fields

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(Received 15 September 1983)

The Hall effect and the magnetoresistance of (TMTSF)₂ClO₄ have been measured at temperatures from 0.08 to 10 K and in magnetic fields to 22 T. The low-temperature data suggest a series of transitions induced by an orbital effect from the magnetic field which progressively reduce the carrier density. Oscillations, apparently Shubnikov-de Haas, also are observed above 10 T and at temperatures up to 10 K.

PACS numbers: 71.25.Hc, 71.30.+h, 72.15.Gd

The (TMTSF)_x family of organic conductors has an intriguing set of phase diagrams in temperature, pressure, magnetic field, and anion composition space. At room temperature these salts are metallic¹ but the ground states vary from metal to superconductor,² spin-density wave (SDW),³ or anion-order-induced charge-density wave (CDW)⁴ depending on the particular anion and the pressure. At low temperature, crystals which remain metallic have extraordinarily large anisotropic magnetotransport coefficients⁵ especially in light of the band structure⁶ which predicts only open orbits. Perhaps the most unusual phenomenon observed in these materials is found only in the metallic state at temperatures below ~10 K. Here, when a magnetic field is applied along the *c** direction, "oscillations" are induced in many of the properties as the field is increased beyond a "threshold field." This effect was first discovered in the PF₆ salt.⁷ Recent work on the ClO₄ salt⁸ has shown that the state found above the "threshold field" is magnetic in character, similar to the SDW state observed in the insulating state.⁹ However, a detailed understanding of the nature of the field-induced state and exactly how the magnetic field induces such a state is

lacking.

To learn more about the field-induced state we have made the first measurements of the Hall effect and magnetoresistance in (TMTSF)₂ClO₄ at fields up to 22 T and temperature down to 80 mK.¹⁰ The Hall data at 80 mK correspond to an effective carrier concentration at 15 T which is ~200 times smaller than that calculated from the stoichiometry. However, this apparent decrease in carriers does not appear abruptly above the onset field but occurs as a series of steps, as one would expect from a series of transitions to semimetallic states with increasingly lower electron density.

Another important finding is the presence of "real" Shubnikov-de Haas (SdH) oscillations above 10 T. These oscillations appear even above 5 K, where no threshold can be identified. The frequency of the oscillations suggests the presence of closed orbits encompassing 3.4% of the Brillouin-zone *a-b* plane.

The experiments were performed in two apparatus at the Francis Bitter National Magnet Laboratory. One setup used a He³ cryostat capable of 0.5 K in conjunction with a 22 T magnet and the other a dilution refrigerator capable of 80 mK

in a 15 T magnet. The samples were mounted on 13- or 25- μm gold wires with Ag paint. Two current leads were placed on the ends of the rectangular platelike crystals (current along the highly conducting a axis) and two additional leads were placed on each of the long edges of the samples so that the Hall effect (a - b plane) and magnetoresistance could be obtained simultaneously. Hall measurements were done at 27 Hz with typical currents of $\sim 500 \mu\text{A}$ and resulting maximum voltages of $250 \mu\text{V}$ at low temperature and high field. Typical sample dimensions were $5 \text{ mm} \times 0.3 \text{ mm} \times 35 \mu\text{m}$. The samples were aligned by eye so that the magnetic field was parallel to the crystallographic c axis.

$(\text{TMTSF})_2\text{ClO}_4$ is superconducting and has large magnetotransport coefficients at low temperatures only when it is slowly cooled through the anion-ordering temperature (24 K).^{9,11} Quick cooling ("quenching") results in a SDW transition at $\sim 5 \text{ K}$.¹¹ The present samples were cooled from 40 to 4 K at a rate of less than $\frac{1}{2} \text{ K/min}$, and showed a monotonic decrease in resistance as temperature was lowered from 40 to 0.08 K.

In Fig. 1 we show the resistance measured in the magnetoresistance and Hall configurations plotted versus applied field. At 0.5 K the magnetoresistance is substantial, but the Hall resistance R_{xy} is too small for our sensitivity, up to the threshold field ($\sim 5 \text{ T}$). Above this field the resistance increases more rapidly and the Hall coefficient becomes observable. R_{xx} remains small until 6.4 T at which point there is another rapid increase and leveling off until 8 T. At this point R_{xy} again rapidly increases and then remains fairly level above 12 T. This behavior in

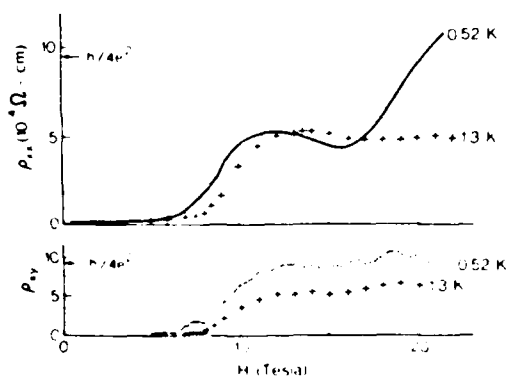


FIG. 1. Magnetoresistance and Hall resistance as functions of magnetic field at 0.52 and 1.3 K. Resistance is also labeled in terms of h/e^2 per conducting plane. At 0.52 K, $R_{xx}(20 \text{ T})/R_{xx}(2 \text{ T}) \sim 250$.

R_{xy} is characteristically different from the variations about a straight line ($R_{xy} \propto H$) which would be expected for the SdH effect or the quantum Hall effect (QHE).¹² On the other hand 80-mK data (Fig. 2), which show five jumps between 3.25 and 8 T, indicate that the jump positions are roughly periodic in $1/H$ with a frequency of $\sim 23 \text{ T}$. (We note that an expected Hall jump at 11.4 T is conspicuously absent.)

We have measured three samples to 0.5 K and 22 T and two samples to 80 mK at 15 T. All of these samples showed the same Hall resistance to within our uncertainty of orientation and sample dimensions ($\pm 15\%$). The sharp increase in R_{xy} suggests some manifestation of the QHE. For comparison we have indicated the Hall resistivity in terms of h/e^2 per conducting plane in Fig. 1. However, the non-integer ratio of the plateaus of R_{xy} , the temperature dependence, and the absence of a significant lowering of R_{xx} indicate that a single-carrier QHE is not sufficient to explain our results.

The Hall coefficient is positive and gives the effective number of carriers as $7 \times 10^{18} \text{ holes/cm}^3$ at 20 T and 0.5 K. This value is both field and temperature dependent as shown in Fig. 3.

The threshold field versus temperature for all measurements on all of the samples used in this study is shown in the upper inset of Fig. 4. Previous limited measurements agree with the present more extensive data. The washing out of the magnetic-field-induced transition above 5 K is illustrated by the data shown in Fig. 4, where we have plotted the magnetoresistance at temperatures of 4, 7, and 10 K. What is even more intriguing in this figure are the oscillations of the resistance, seen at high fields at all of the temperatures shown as well as at lower temperatures. The positions of the maxima in these os-

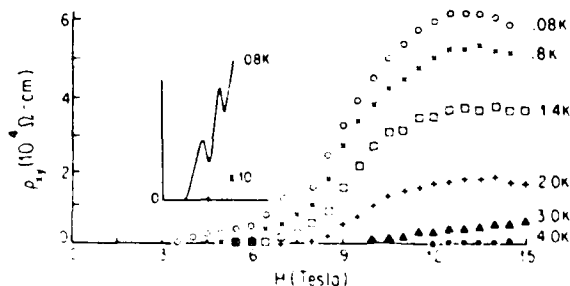


FIG. 2. Hall resistance vs magnetic field at several temperatures for another sample. Inset is an enlargement of the threshold region.

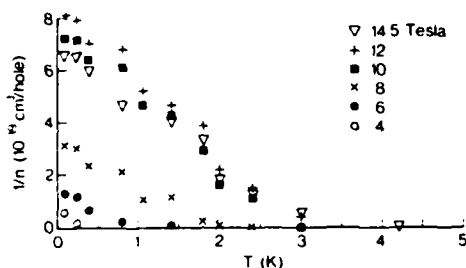


FIG. 3. Temperature dependence of the Hall coefficient (plotted as inverse effective carrier density) at various fields.

cillations plotted vs $1/H$ (lower inset Fig. 4) yield a straight line characteristic of the SdH effect with a frequency of 275 ± 15 T. This frequency is ~ 10 times the frequency seen in the vicinity of the threshold field, but is very similar to one of the frequencies reported by Bando *et al.* (More often we saw a frequency of 550 T which we take as a harmonic.)

Current interpretations of the low-temperature, high-field behavior suggest that the threshold field signals a sharp transition from either open orbits to closed orbits, or from very small closed orbits to somewhat larger ones, and this is followed by "conventional" SdH oscillations.^{7, 3, 10, 14} The present study of $(\text{TMTSF})_2\text{ClO}_4$ suggests that here the threshold field initiates a series of transitions, approximately periodic in $1/H$ (below 10 T), which progressively reduce the effective number of carriers. This interpretation is consistent with the shape and hysteresis of the magnetoresistance (observed in the present work as well as previously reported⁹), and the measured ^{77}Se NMR relaxation rates,^{9, 15} and sound velocity¹⁶ which show that the density of states at the Fermi surface is reduced in a roughly stepwise manner as magnetic field is increased. We note that much of this anomalous behavior has not been observed in the PF_6 salt which also has a threshold field. The high-frequency oscillations we observe may be related to the oscillations observed in the PF_6 salt. The frequency is close to that predicted for $(2k_F, 0, 0)$ nesting of the Fermi surface,¹¹ neglecting anion ordering.

The threshold field depends uniquely on the component of the field along the c axis.^{7, 13, 15} Thus, unless there are enormous spin-orbit effects, the transitions are induced by an orbital effect of the magnetic field rather than spin alignment.¹¹ The orbital nature of these effects is also suggested by the approximate $1/H$ dependence found here.

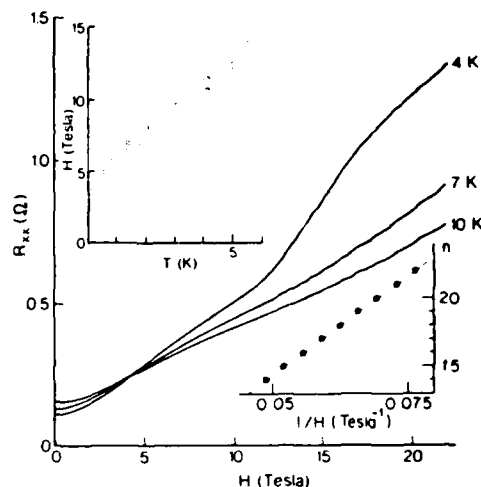


FIG. 4. Magnetoresistance vs magnetic field at 4, 7, and 10 K. Note oscillations at high field. Upper inset: Temperature dependence of the threshold field for all of the samples investigated in this study. Lower inset: Positions of the maxima from the 7 K data vs $1/H$.

Such orbitally induced transitions are not common. The only similar effect is the proposed CDW transition in graphite at low temperatures and in sufficient fields so that it is almost in the extreme quantum limit.¹⁷ In such large fields the electronic structure consists of a series of distinct Landau levels each described by the quasi one-dimensional dispersion and density of states of the narrow c -axis band.^{18, 19} The one-dimensional band structure is susceptible to a number of distortions at $2k_F$ along c , of which, for graphite, the proposed strongest is due to a Coulomb-induced CDW.¹⁸ The temperature dependence of the observed and predicted transition in graphite is similar to the temperature dependence of the threshold field in the present case. The dominant effect in $(\text{TMTSF})_2\text{ClO}_4$, however, is probably some form of SDW.^{9, 15} The approximate $1/H$ dependence of the transitions may result from the presence of several Landau levels below the Fermi energy when the threshold field is first reached at low temperature.¹⁹

In conclusion we have shown that the Hall resistance increases in a roughly stepwise manner as magnetic field is increased past a threshold at low temperature, and we suggest that this is the result of a series of transitions induced by the orbital motion of the carriers in the applied field. We also observe apparent SdH oscillations at high

field suggesting the presence of closed orbits with area $\sim 3.4 \bar{c}$ of the a - b plane of the Brillouin zone.

We would like to acknowledge the hospitality of the Francis Bitter National Magnet Laboratory where these experiments were performed. We would also like to thank Victor Lee for preparing the samples and M. Ya. Azbel, S. Alexander, T. Holstein, and P. Pincus for useful discussions. This work was supported by the National Science Foundation through Grants No. DMR81-15241 and No. DMR81-13456 and the U. S. Department of Energy under Contract No. DEAC04-76-DP00789.

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Superconductivity in a New Family of Organic Conductors

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Evidence for superconductivity in $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ [where BEDT-TTF is *bis*(ethylenedithiolotetrathiafulvalene)] near 2 K for pressures above 4 kbar is reported. This is the first unambiguous observation of superconductivity in a sulfur-donor organic system. At higher pressures the transition temperature decreases rapidly, $dT_c/dP \sim -0.3$ K/kbar. At low pressures this material exhibits a first-order metal-insulator transition, postulated to result from a change in the arrangement of the anions which are ordered at room temperature.

PACS numbers: 74.10.+v, 61.65.+d, 71.30.+h, 72.15.Eb

We report the discovery of superconductivity in a new family of organic conductors based on a sulfur-donor organic molecule. This is only the second organic system in which superconductivity has been observed. The overwhelming majority of organic conductors are unstable at low temperatures to periodic lattice distortions leading to an insulating ground state.¹ Over the past decade extensive studies on a wide range of structural and chemical types of organic linear-chain systems were carried out with the important aim of suppressing these instabilities and stabilizing a

low-temperature metallic or superconducting state. Recently this goal was finally achieved for several members of the $(\text{TMTSeF})_2X$ family of compounds (where TMTSeF is tetramethyltetraselenafulvalene and X is, for example, FF_6 , TaF_6 , ReO_4 , ClO_4) with the observation of superconductivity near ~ 1 K for pressures above some critical pressure, $P_c \sim 1$ bar to 12 kbar.²⁻⁵ The reason why these particular compounds become superconducting is unclear, although it may be related to their atypical crystal and chemical structure. Indeed the related isostructural series

of materials, $(\text{TMTTF})_2X$ (the TMTTF molecule is identical to TMTSeF but with the Se replaced by S) has similar phase diagrams but with substantially higher P_c (~ 25 – 45 kbar) and no conclusive evidence of superconductivity.^{6,7} It is therefore clearly of interest to find other organic systems which are superconducting in order to better understand the mechanism for organic superconductivity and perhaps raise T_c .

Recently Saito *et al.*⁸ prepared a ClO_4 salt of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) with inclusion of some solvent in the crystal structure. Concurrently we have electrochemically⁵ synthesized various salts of BEDT-TTF.⁹ Of interest here are the ReO_4 salts. A number of distinct crystallographic phases were obtained and characterized by x-ray crystallography, chemical analysis, and ESR. From tetrahydrofuran (THF) three phases were found; thin needles of chemical formula $(\text{BEDT-TTF})_4(\text{ReO}_4)_2(\text{THF})$, and two phases growing as plates of form $(\text{BEDT-TTF})_6(\text{ReO}_4)_4$ and $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$. All three phases could easily be identified from their distinct morphologies. Chemical and x-ray analysis show that neither plate phase includes solvent. The electrical properties and behavior under pressure of these phases are very different.

The 4:2 salt $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ becomes superconducting below ~ 2 K for pressures above ~ 4 kbar. In Fig. 1 we present evidence for superconductivity in this compound from four-probe resistance measurements at 7 kbar as a function of magnetic field. The resistance drops to zero within experimental accuracy below the transi-

tion; $T_c \sim 1.4$ K, defined as that temperature where R is half the normal value. At 4 kbar we observe an onset of superconductivity near 2 K although the transition is considerably broadened. The possibility that the superconductivity we observe is filamentary can be ruled out because we measure critical current densities of order 0.1 A/mm², which are comparable to those found in the $(\text{TMTSeF})_2X$ superconductors² for which the bulk nature of this phenomenon is well established⁵.

The structure of $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ is shown in Fig. 2 and bears some similarity to that of the $(\text{TMTSeF})_2X$ salts.⁵ In particular the BEDT-TTF molecules are "zig-zagged" along the a axis, providing cages in which the ReO_4 anions sit and so determining the stoichiometry of the material; there is the possibility of strong S-S bonding between BEDT-TTF molecules along the b direction but direct interactions between these molecules in the c direction are clearly much weaker (note that the BEDT-TTF molecule contains twice as many S atoms as the TMTTF molecule). The structure belongs to space group $P\bar{1}$ with unit cell $a = 7.78$ Å, $b = 12.59$ Å, $c = 16.97$ Å, $\alpha = 73.01^\circ$, $\beta = 79.89^\circ$, $\gamma = 89.06^\circ$, $V = 1565$ Å³. However, there are two important differences compared with the structure of the $(\text{TMTSeF})_2X$ salts.^{5,10} Firstly, whereas the TMTSeF molecule is almost planar, the terminal

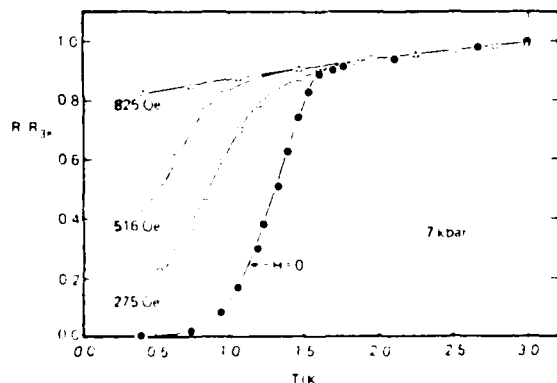


FIG. 1. Resistance [normalized to $R(3\text{ K})$] vs temperature curves along the a axis of $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ in zero field and for various magnetic fields applied along the transverse c^* direction.

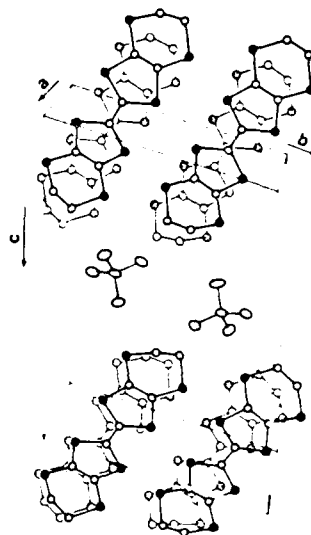


FIG. 2. Projected left-eye view of the structure of $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ along the organic molecular stacking axis, a , showing the BEDT-TTF molecules (shaded and open circles correspond to S and C atoms, respectively; H atoms are not shown) and ReO_4 anions.

methylene (CH_2) groups at either end of the BEDT-TTF molecule are positioned well out of the plane of the rest of the molecule. Secondly, the ReO_4^- anions are ordered at room temperature; in none of the $(\text{TMTSeF})_2\text{X}$ salts is this the case.⁵

The room-temperature a -axis conductivity of $(\text{BEDT-TTF})_2(\text{ReO}_4)_2$ at 1 bar is $\sim 200 (\Omega \text{ cm})^{-1}$, comparable to the most conducting of the $(\text{TMTTF})_2\text{X}$ salts.¹¹ Conductivity was measured with use of a standard four-probe lock-in technique, with silver paint contacts of resistance a few ohms. Data at 1 bar are shown in Fig. 3; the material shows metallic behavior to 81 K where there is a metal-insulator (MI) transition. The resistance abruptly increases by two orders of magnitude at T_{MI} demonstrating that the transition is of predominantly first-order character. The resistance is activated below the transition with an activation energy, Δ , given by $2\Delta/kT_{\text{MI}} \sim 13$. Measurements of conductivity anisotropy in the a - b plane were made with the Montgomery geometry giving a value at 300 K of $\sigma_a/\sigma_b \sim 20$. This ratio varies little as the temperature is decreased to T_{MI} , and is comparable with the generally agreed value of the analogous anisotropy ratio in the $(\text{TMTSeF})_2\text{X}$ salts.⁵ Measurements were made as a function of pressure in a simple Be-Cu piston cylinder clamp cell, with the sam-

ples contained in a Teflon cell filled with heptane. As pressure is increased the MI transition temperature falls and above ~ 7 kbar is suppressed. A resistance curve at 7 kbar is given in Fig. 3 with data below 3 K shown earlier in Fig. 1. The sample has a high resistance ratio of ~ 300 , indicative of good crystal quality. The resistance does not saturate at low temperatures but continues to fall to ~ 2 K below which temperature the resistance drops to zero as previously described. The normal resistance is restored with the application of a magnetic field. Data are shown in Fig. 1 for field applied along the c^* direction, giving a critical field of ~ 800 G. The critical field is about 2 times higher in the b^* direction. All these features are also seen in the $(\text{TMTSeF})_2\text{X}$ materials to a similar degree. There is a substantial transverse magnetoresistance, but in contrast with the $(\text{TMTSeF})_2\text{X}$ salts it is largest along the b^* direction. These results will be described in more detail elsewhere. Similar results have been seen in about a dozen crystals for various applied pressures and are summarized in the phase diagram shown in Fig. 4. In particular the superconducting transition temperature falls rapidly with pressure ($dT_c/dP \sim -0.3$ K/kbar). This is a very unusual effect whose origin is unclear. The phase diagram suggests that T_c is somewhat depressed in the critical region (4–6 kbar) perhaps through competi-

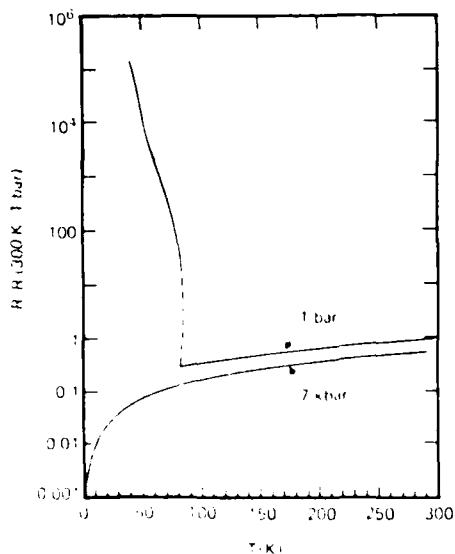


FIG. 3. Resistance vs temperature curves for $(\text{BEDT-TTF})_2(\text{ReO}_4)_2$ at 1 bar and 7 kbar. The resistance is normalized with respect to $R(300 \text{ K}, 1 \text{ bar})$ and a value of $d\sigma/dP$ of 20% /kbar has been used to normalize the high-pressure data.

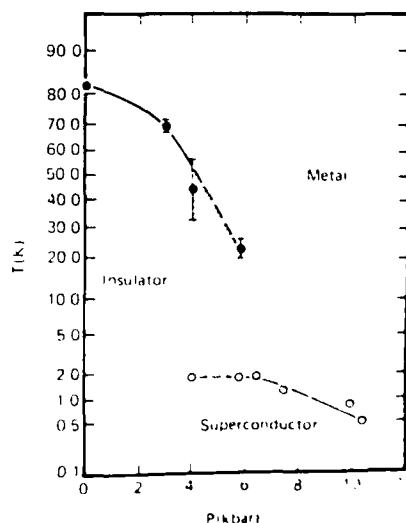


FIG. 4. Phase diagram of $(\text{BEDT-TTF})_2(\text{ReO}_4)_2$. The shaded region corresponds to that in which large hysteresis is observed on cooling and warming. The open circles correspond to onset of superconductivity.

tion with anion ordering, a mechanism previously postulated in the $(\text{TMTSeF})_2\text{X}$ system.³ For pressures close to 6 kbar there can be a substantial increase in resistance well above T_c and the superconducting transition is considerably broadened. Moreover in this pressure region the resistance shows substantial hysteretic effects similar to those previously seen in $(\text{TMTSeF})_2\text{ReO}_4$ (Ref. 12) and associated with anion ordering. Changes in the ESR spectrum at T_{MI} are also similar to those seen at anion ordering transitions in the $[\text{TMTSe}(\text{T})\text{F}]_2\text{X}$ salts. It thus seems likely that the MI transition seen below ~ 7 kbar in the BEDT-TTF salt is associated with some kind of anion rearrangement, consistent with the high value of $2\Delta/kT$ mentioned above.

In summary, we have found superconductivity in a member of a new class of organic conductors based on a sulfur donor, BEDT-TTF. At low pressures $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ exhibits a metal-insulator transition which we suggest is associated with some kind of anion rearrangement. Above and in a critical pressure regime (~ 4 – 6 kbar) superconductivity is observed with onset of superconductivity near 2 K at the lowest pressures. T_c is depressed in the critical pressure regime perhaps through competition with the low-pressure insulating instability and thus the possibility of higher superconducting transition temperatures in other BEDT-TTF salts cannot be ruled out. The variety of BEDT-TTF:X phases may permit the correlation of the existence of superconductivity with a particular structural type. This is an important distinction from the $(\text{TMTSeF})_2\text{X}$ family of compounds for which only a single phase is known.

We thank J. Voiron for experimental input and J. Vazquez and A. Schweiger for their technical assistance. The Molecular Structure Corpora-

tion carried out the structure determination of $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$. This work was supported in part by the U. S. Office of Naval Research.

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A SULPHUR BASED ORGANIC MOLECULAR SUPERCONDUCTOR : $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$

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Résumé — Nous avons préparé un certain nombre de sels de la molécule organique, BEDT-TTF, dérivée du soufre avec divers anions dont ReO_4 , ClO_4 , BF_4 , PF_6 et Br. Pour le même anion, on trouve des sels avec différentes stœchiométries. Pour l'anion ReO_4 , nous avons à présent identifié trois phases différentes. Le sel 2:1, soit $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$, devient supraconducteur pour des pressions supérieures à 4 kbar avec une température de transition aux environs de 2 K. A plus haute pression, T_c décroît rapidement à un taux, dT_c/dP de $-0,3$ K/kbar. A plus basse pression ce sel présente une transition métal-isolant du premier ordre, près de 80 K. Nous suggérons que cette transition est associée à un réarrangement des anions ReO_4 qui sont ordonnés à température ambiante.

Abstract — We have prepared a number of salts of the sulphur derived organic molecule, BEDT-TTF, with various anions including ReO_4 , ClO_4 , BF_4 , PF_6 and Br. For the same anion, salts with various stoichiometries are found. For the ReO_4 anion, we have so far identified four different phases. The 2:1 salt, $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$, becomes superconducting for pressures above ~ 4 kbar with a transition temperature near 2K. At higher pressures, T_c falls rapidly at a rate, $dT_c/dP \sim -0.3$ K/kbar. At lower pressures this salt exhibits a first order metal-insulator transition near 80 K which we suggest is associated with a rearrangement of the ReO_4 anions which are ordered at room temperature.

1: Introduction

In this paper we review our recent finding /1/ of superconductivity near 2 K in $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$, (where BEDT-TTF is the bis(ethylenedithio)tetrafulvalene molecule /2/), for pressures above 4 kbar. For over a decade the possibility of finding superconductivity in an organic material has been the 'holy grail' of numerous physicists and chemists. Although possibly several hundred organic molecular chain systems have been studied /3/, the BEDT-TTF salts form only the second family of organic molecular superconductors; the First Family, so to speak, being the $(\text{TMTSeF})_2\text{X}$ family /4-6/†, for which, at present, 6 or 7 members are known to become superconducting above some critical pressure, P_c /5,6/, all with T_c close to 1 K at P_c . The origin and nature of the superconducting state in the $(\text{TMTSeF})_2\text{X}$ materials, although well characterised, is the subject of much controversy (see, for example /4,7/). The discovery of superconductivity in the (BEDT-TTF) salts may be expected to be important in finding answers to some of these questions. Moreover, as we shall discuss further below, the BEDT-TTF molecule forms salts with a variety of crystal structures and stoichiometries, unlike the $(\text{TMTSeF})_2\text{X}$ salts, enabling the possible correlation of superconductivity with, for example, a particular structural type, or a particular stoichiometry and associated band filling.

† The related family of linear chain conductors, $(\text{TMTTF})_2\text{X}$, based on the sulphur derived molecule, TMTTF, become highly conducting under pressures above 25-45 kbar and show metallic behaviour to low temperatures /7,8/. Although a possible resistive superconducting transition near 3 K was reported in $(\text{TMTTF})_2\text{Br}$ at 25 kbar /7/, later more extensive resistivity studies on about 100 samples showed this behaviour was dependent on sample batch, with different temperature dependences of the resistivity at low temperatures in samples of $(\text{TMTTF})_2\text{Br}$ grown by two different groups /8/. No convincing evidence for superconductivity was found in this study.

Conductivity of the BEDT-TTF salts was measured using a low frequency lock-in technique, with silver paint contacts arranged 4-in-line along the length of the crystals. Contact resistances were generally a few ohms. The room temperature conductivity of $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ at 1 bar is about $200 (\Omega\text{cm})^{-1}$. At 1 bar the material shows metallic behaviour to 81 K where there is a dramatic metal-insulator (M-I) phase transition (figure 2(a)). At this temperature the resistance increases abruptly by several orders of magnitude clearly demonstrating the first-order character of the transition. Below $T_{\text{M-I}}$ the resistance exhibits an activated behaviour with an energy gap, $2\Delta \sim 1050$ K. Data was taken as a function of pressure using a simple Be-Cu piston cylinder clamp cell. The pressure-transmitting fluid used was heptane contained within a teflon cell. As the pressure is increased $T_{\text{M-I}}$ drops as shown in figure 2(b), and above 7 kbar the M-I transition is completely suppressed. A resistance curve at 7 kbar is given in figure 2(a) with data below 3 K shown in figure 3 as a function of magnetic field. Figure 3 reveals clear evidence for a superconducting transition at 7 kbar with a transition temperature, $T_c \sim 1.4$ K (where T_c is defined as that temperature where the sample resistance has fallen to half the normal value just above T_c). The resistance goes to zero, within experimental accuracy, below T_c . Application of a magnetic field restores the normal resistance, with a critical field along the c^* axis of ~ 800 G. The critical field is about twice as large along the b^* direction. The samples exhibit excellent resistance ratios indicating high crystal quality. For the sample in figure 3 the resistance ratio is about 300. Note that the normal resistance does not saturate at low temperatures but continues to fall to T_c where the resistance drops to zero, as previously described. All these features are also displayed by the $(\text{TMTSeF})_2\text{X}$ materials to a similar extent /13/. Moreover $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ exhibits a substantial magnetoresistance at low temperatures, but in contrast with the $(\text{TMTSeF})_2\text{X}$ salts is largest along the b^* direction.

We observe superconductivity at lower pressures, as shown in the phase diagram in figure 2(b). Figure 2(b) contains results from more than a dozen crystals, in which evidence for superconductivity similar to that shown in figure 3 has been found. At 4 kbar we observe onset of superconductivity near 2 K, although the transition is considerably broadened. The possibility that the superconductivity we observe is filamentary can be ruled out because we measure critical current densities of order 0.1 A/mm^2 , which are comparable to those found in the $(\text{TMTSeF})_2\text{X}$ superconductors, for which the bulk nature of the superconductivity is now well established /12/. The superconducting transition temperature falls rapidly with pressure ($dT_c/dP \sim -0.3 \text{ K/kbar}$), at a rate about 3 times that observed in the $(\text{TMTSeF})_2$ salts /5,6/. The explanation of this effect is unclear. The phase diagram suggests that T_c is somewhat depressed in the critical region (4-6 kbar) perhaps through competition with anion ordering, a mechanism previously postulated in the $(\text{TMTSeF})_2\text{X}$ system /6/. Moreover, by extrapolation of the normal-superconducting phase boundary to lower pressures in figure 3, a superconducting transition temperature as high as 5 K seems quite possible if the anion ordering could be suppressed at even lower pressures. One possibility is by replacing the ReO_4 anion with a large centrosymmetric anion.

As mentioned above the superconducting transition is broadened for a narrow pressure range extending from ~ 4 to ~ 6 kbar. For these pressures the resistance can increase considerably above T_c with a minimum in resistance for temperatures as high as 20-30 K. We observe hysteretic effects at these pressures with, for example, the possibility of increasing the sample resistance through temperature cycling. This behaviour is similar to that seen in $(\text{TMTSeF})_2\text{ReO}_4$ /14/ and other TMTSeF and TMTTF salts /15/ under pressure and is associated with anion ordering transitions. It thus seems likely that the M-I transition seen in at low pressures is associated with some kind of anion rearrangement, consistent with the high value of $2\Delta/kT$ mentioned above.

Other BEDT-TTF phases

Crystals of the BEDT-TTF salts were obtained using a range of different solvents, including tetrahydrofuran (THF), methylene chloride, acetonitrile and 1,1,2-trichloroethane. A number of distinct crystallographic forms of the ReO_4 salts of BEDT-TTF were obtained, including the 2:1 stoichiometry salt described above. The various phases were characterised using a variety of different techniques, including optical microscopy, x-ray crystallography, chemical analysis and ESR.

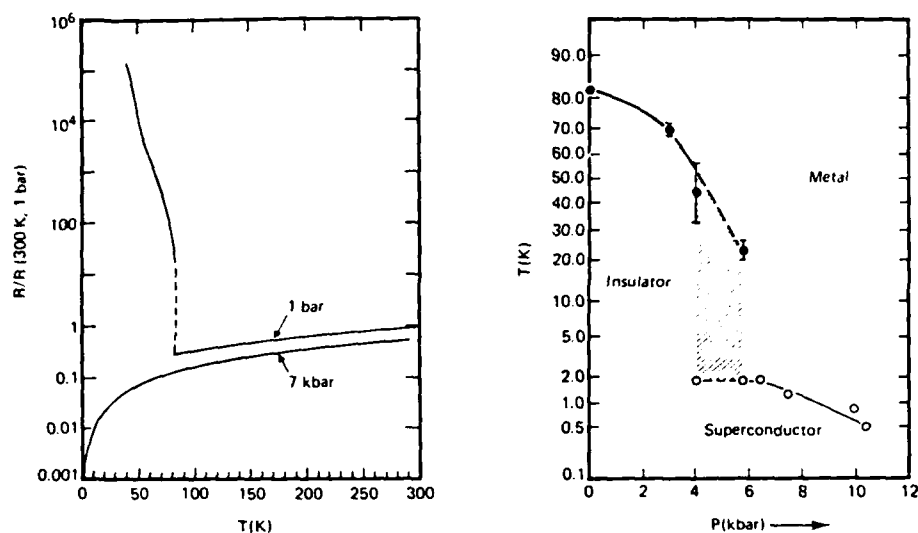


Figure 2: (a) Resistance versus temperature curves for $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ at 1 bar and 7 kbar. The resistance is normalised with respect to $R(300\text{ K}, 1\text{ bar})$ and a value of $d\sigma/dP$ of 20 %/kbar has been used to normalise the high pressure data. (b) Phase diagram of $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$. The shaded region corresponds to that in which large hysteresis is observed on cooling and warming. The open circles correspond to onset of superconductivity.

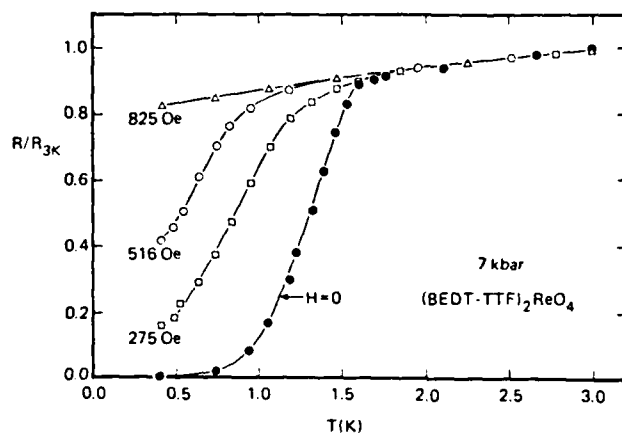


Figure 3: Resistance (normalised to $R(3\text{ K})$) versus temperature curves along the a axis of $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$ in zero field and for various magnetic fields applied along the transverse c^* direction.

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From THF three phases were found; thin needles of probable chemical formula $(\text{BEDT-TTF})_4(\text{ReO}_4)_2(\text{THF})$ and two phases growing as plates of form $(\text{BEDT-TTF})_6(\text{ReO}_4)_4$ and $(\text{BEDT-TTF})_4(\text{ReO}_4)_2$. The latter two phases have very similar habits, but there are sufficient characteristic differences between the phases that they can be identified unambiguously from a trivial optical examination. Both chemical and x-ray analysis show that neither phase includes solvent. In contrast chemical analysis suggests there is incorporation of solvent in the needle phase. Single crystal x-ray determination of the structure of this phase was not possible because of the very poor quality of the crystals, which were mostly twisted. Room temperature structural information on some of these phases is given in table 1. As can be seen from table 1, the ReO_4 and ClO_4 salts, with stoichiometry of 3 BEDTTTF molecules to 2 anions, have different crystal structures belonging to different space groups. We have grown several materials which exhibit an activated conductivity behaviour, including the 1:1 BEDTTTF: PF_6 salt, for which some information is given in table 1. More details of these structures will be described elsewhere.

Table 1: Room Temperature Structural Data on Various BEDT-TTF Salts

Stoichiometry	ReO_4 3:2	ReO_4 2:1	ClO_4 3:2	PF_6 1:1
a	8.498	12.596	9.513	33.827
b	30.566	17.117	16.488	6.714
c	9.413	7.802	7.620	8.293
α		99.55	92.90	
β	98.57	90.85	95.98	102.52
γ		73.46	89.13	
Volume (\AA^3)	2417.9	1589.3	1187.2	1838.6
Symmetry	$\text{P2}_1/\text{n}$	P1^*	P1^*	$\text{C2}/\text{c}$
	mono	tri	tri	mono
	clinic	clinic	clinic	clinic
Z	4	2	1	4

Space does not allow a detailed description of other measurements that we have made on various members of the BEDTTTF family of compounds, including thermopower, pressure-temperature phase diagrams, and conductivity data. Brief details of ESR work on three of the ReO_4 phases are given in figure 4. The magnetic properties of the ReO_4 phases as measured by ESR at 1 bar are quite different. For the 2:1 phase both susceptibility, χ , and linewidth of the ESR signal, LW, show an abrupt transition near 90 K, similar to that seen at the anion ordering transition in $(\text{TMTSeF})_2\text{ReO}_4$ /16/. There is a maximum in χ near 100 K, whereas the LW decreases monotonically with temperature.

The 3:2 ReO_4 phase has several interesting ESR features. In particular, as also shown by conductivity studies, the transition is much smoother as compared with the 2:1 phase. The LW displays a broad maximum near 190 K; the susceptibility decreases continuously with temperature. Below the metal-insulator transition two distinct ESR lines are observed, which are presumably associated with the two inequivalent BEDTTTF sheets which make up the structure of the 3:2 phase. The characteristics of both χ and LW are similar to those found for TTF-TCNQ /17/, suggesting the phase transition in the 3:2 phase is also derived from a Peierls instability. Conductivity studies as a function of pressure also indicate the metal-insulator transition in this material has a different character from that found in the 2:1 phase - the M-I transition for the 3:2 phase is much less affected by pressure. The third ReO_4 phase for which data is given in figure 4 is the needle phase mentioned earlier for which we have no structural information. The conductivity of this phase shows no well defined behaviour but is activated and low at 300 K. The ESR linewidth decreases approximately linearly until a Curie susceptibility begins to dominate below ~50 K. Note that the ESR line at low temperatures has the same g-value as at higher temperatures, demonstrating that the Curie tail derives not from independent paramagnetic species but rather from defects in the molecular stacks.

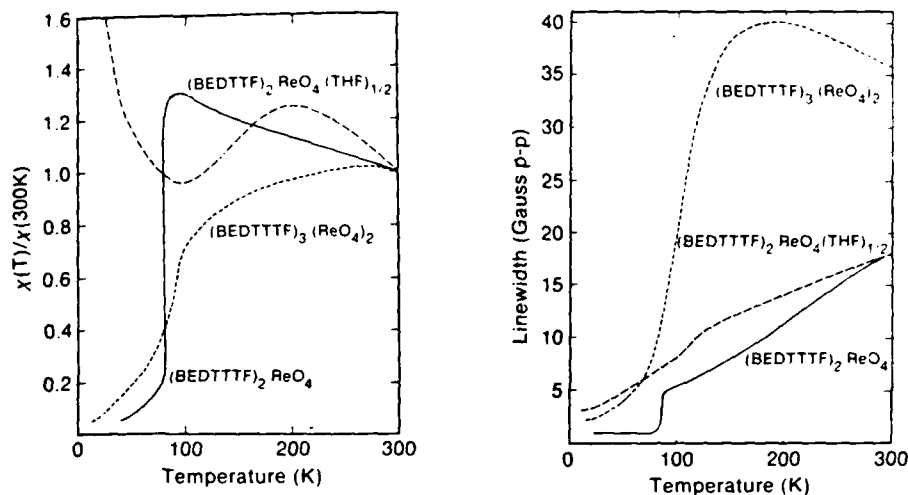


Figure 4: (a) Spin-susceptibility, χ , and (b) ESR linewidth of three phases of $(BEDTTTF) (ReO_4)_x$. χ is normalised to the respective room temperature value.

IV: Conclusions

In summary we have prepared a new class of organic conductors based on a sulphur donor, BEDTTTF. At present we have identified four different crystal structures with stoichiometries of BEDTTTF to anion of 1:1, 3:2 and 2:1. The 3:2 salts display two different crystal structures. Various phases incorporating the same anion are formed. For the ReO_4 anion a number of phases have been found, two of which form plate-like crystals. At low pressures $(BEDTTTF)_4(ReO_4)_2$ exhibits a M-I transition which we suggest is associated with some kind of anion rearrangement. Above and in a critical pressure regime (~4-6 kbar) superconductivity is observed with onset of superconductivity near 2 K at the lowest pressures. T_c is depressed in the critical pressure regime perhaps through competition with the low pressure insulating instability. We believe there is a strong possibility of higher superconducting transition temperatures in other BEDT-TTF salts for which the low pressure insulating phase is suppressed. The 3:2 BEDTTTF ReO_4 salt shows a much less abrupt M-I transition as compared with the 2:1 salt both at 1 bar and under pressure. ESR data suggest this transition originates from a Peierls instability.

The large array of BEDT-TTF:X phases will allow improved understanding of the origin of superconductivity and lattice instabilities in organic conductors by correlating these properties with structural characteristics of the various BEDTTTF phases. This is an important distinction from the $(TMTSeF)_2X$ family of compounds which usually form a single phase.

We thank J. Vazquez and A. Schweiger for their technical assistance. The Molecular Structure Corporation carried out the structure determination of $(BEDT-TTF)_4(ReO_4)_2$. This work was partially supported by the U.S. Office of Naval Research.

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FAR INFRARED PROPERTIES OF $(\text{TMTSF})_2 \text{ClO}_4$ W.A. Chailener, P.L. Richards and R.L. Greene^{*}*University of California and MMRD, Lawrence Berkeley Laboratory,
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Résumé - La réflectance de $(\text{TMTSF})_2 \text{ClO}_4$ a été mesurée entre 4 et 40 cm^{-1} . À 2K deux pics étroits sont observés à 7 et 29 cm^{-1} . Entre 2K et 80K l'intensité des pics diminue mais leur fréquence ne change pas. Sous irradiation de rayons X l'intensité des pics diminue également. Un champ magnétique (jusqu'à 40 kOe) appliqué le long de l'axe c^* ne change pas le pic à 29 cm^{-1} . Ces expériences suggèrent que les pics proviennent des vibrations moléculaires couplées aux électrons. Ces expériences sont incompatibles avec l'interprétation expliquant l'origine /1/ du pic à 29 cm^{-1} par un pseudogap supraconducteur.

Abstract - The far infrared properties of $(\text{TMTSF})_2 \text{ClO}_4$ have been measured for frequencies between 4 and 40 cm^{-1} . At 2K, phonon-like peaks in reflectance are seen at 7 and 29 cm^{-1} . Increasing the temperature to 80K causes these peaks to gradually disappear, but not to shift appreciably in frequency. Radiation-induced defects substantially reduce the height of the 29 cm^{-1} peak. Experiments at 2.3K and 4.2K show no change in the 29 cm^{-1} peak with a magnetic field of up to 40 kG applied parallel to the c^* -axis. These results suggest a coupled electronic-molecular vibration origin for these features. They are incompatible with the recently proposed /1/ interpretation of the 29 cm^{-1} feature as a quasi-one-dimensional superconductive pseudogap.

Introduction

The charge transfer compound $(\text{TMTSF})_2 \text{ClO}_4$ is the first organic conductor which becomes superconducting at ambient pressure (with $T_c \sim 1\text{K}$). Because of the unusual properties of this, and related salts based on the TMTSF complex, the nature of the highly conducting metallic state above T_c is still a matter of controversy. One hypothesis /2/ suggests the picture of highly mobile carriers with a two-dimensional band structure, while an alternate viewpoint /3/ suggests a form of quasi-one-dimensional superconductivity.

In order to examine these questions we have made far infrared (FIR) measurements on samples of $(\text{TMTSF})_2 \text{ClO}_4$ grown at IBM. We used a conventional Michelson Fourier transform spectrometer with mylar beamsplitters and a composite doped-Ge bolometer operated at 1.2K. The experimental apparatus has been described in detail elsewhere /4/. Reflectance measurements were made on a 0.5 cm^2 mosaic of about ten optically aligned fibers. The fibers were attached to a sheet of black epoxy resin with vacuum grease to insure good thermal contact. This in turn was cemented to a rotatable brass sample wheel. A carbon resistor and heater attached to the wheel were used to monitor and control the sample temperature. The entire assembly was located in an evacuable chamber in a liquid helium bath so that the sample temperature could be varied from 2K to over 100K. The radiation was incident at 7.5° from the normal. The spectra were normalized by using a brass reflector which could be rotated into the sample position.

Transmittance measurements were made on a similar sample mosaic. In this case, fibers were attached with vacuum grease to a copper grid polarizer on a mylar substrate. The fibers were oriented perpendicular to the polarizer grid so that a crossed-grid arrangement was produced [1]. In this way the E-field of the transmitted light was forced by the copper grid to be parallel to the fiber axis of the $(\text{TMTSF})_2\text{ClO}_4$. Fibers were placed in contact with each other to minimize light leakage. The average transmittance of the sample from 4 to 40 cm^{-1} was about 5%. The grid constant of the copper polarizer was $3.8\text{ }\mu\text{m}$ and the mylar substrate had a thickness of $4\text{ }\mu\text{m}$. Both of these dimensions are much less than the wavelengths of the FIR radiation involved. Fiber dimensions, on the other hand, as well as random inter-fiber spacings were comparable to the FIR wavelengths, so interference structure was observed which could be removed by computing ratios of spectra measured at different temperatures or magnetic fields.

The transmittance sample was mounted in an evacuable chamber inside a superconducting magnet and its temperature could be varied from 2.3K to over 100K. A carbon resistor attached to the brass light pipe surrounding the sample monitored the sample temperature. Exchange gas was used to obtain the lowest temperatures (below 20K) and to insure good thermal contact between the sample and thermometer. The magnetic field was oriented perpendicular to the broadest face of the crystal fibers, which was thought to be parallel to the c^* -axis for most of the fibers in the mosaic.

Data

The initial FIR reflectance measurements [5], made as a function of temperature, showed phonon-like peaks at 7 and 29 cm^{-1} (0.9 and 3.6 meV) which were present at and below 60K (Fig.1). The reflectance peaks had widths of 3 to 5 cm^{-1} fwhm with

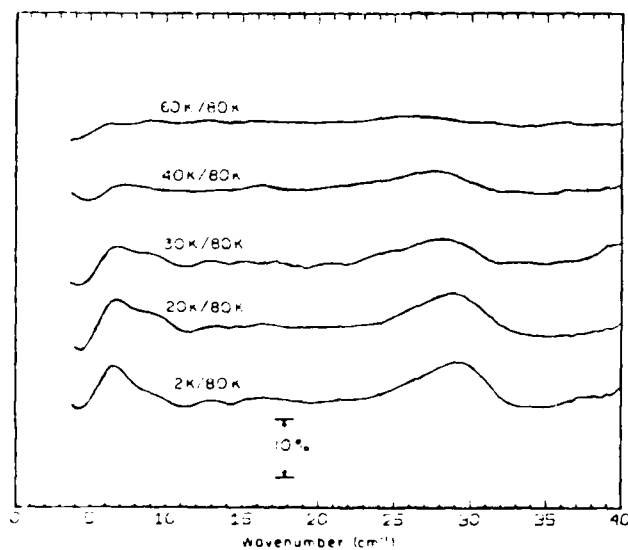


Fig. 1 - FIR reflectance vs. temperature of $(\text{TMTSF})_2\text{ClO}_4$, showing peaks at 7 and 29 cm^{-1} .

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In order to see the feature in the transmittance spectrum at different temperatures and its transmittance feature in the magnetic field and the transmittance sample was cooled at the limit set by an applied field of 10 and 40 kG.

Fig. 2 - FIR transmittance spectrum at

peak heights at 2K of 8% of the background reflectance. Above 20K the peaks gradually disappeared. A sample-in/sample-out normalization procedure determined definitely that the peaks were present at low temperatures, rather than at high temperatures (a fact which cannot be established from ratios of spectra measured at different temperatures).

In order to search for magnetic field dependence, the transmittance of the $(\text{TMTSF})_2 \text{ClO}_4$ sample with the crossed-grid arrangement was first measured at high temperatures (above 40K). The sample was then cooled to liquid helium temperatures, and its transmittance measured again, thereby verifying the presence of the 29 cm^{-1} feature in the low temperature spectrum. With the sample still at this temperature, magnetic fields of 2 to 40 kG were applied parallel to the c^* -axis of the fibers, and the transmittance of the sample was re-measured. Finally, the transmittance of the sample was measured in zero magnetic field, after warming the sample above 40K. The results of one such experiment are shown in Fig. 2. In this case, the sample was cooled at 0.3 K/min from 40K to 15K, before cooling more quickly to 2.3K. To the limit set by the noise level ($\sim 1\%$) there is no change in the 29 cm^{-1} feature in an applied field of 10 kG. A similar null result was found in applied fields of 2, 10 and 40 kG with the sample at 4.2K after quenching from 77K in about one minute.

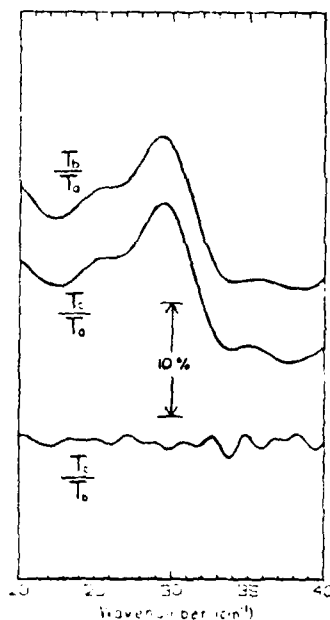
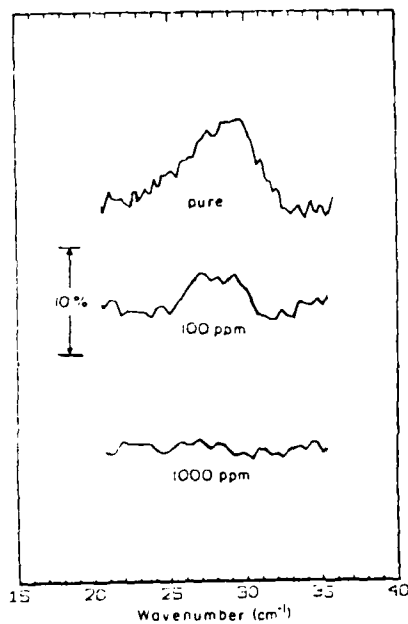


Fig. 2 - FIR transmittance ratios, showing no effect of magnetic field on the 29 cm^{-1} feature. T_a is a transmittance spectrum at $\sim 80 \text{ K}$ in zero applied field. T_i is a transmittance spectrum at 2.3K in zero applied field. T_e is a transmittance spectrum at 2.3K with a 10kG field applied parallel to the c^* -axis of the crystals.

After cycling these samples many times in temperature, the height of the 29 cm^{-1} reflectance peak was found to decrease substantially. This was possibly a result of surface degradation. However, no significant change in peak height with temperature cycling was found in transmittance experiments using the $(\text{TMTSF})_2\text{ClO}_4$ samples in the crossed-grid arrangement.

The effect of x-ray induced defects upon the 29 cm^{-1} reflectance peak was also studied (Fig. 3). Measurements were made of the reflectance of virgin crystals, crystals with ~ 100 ppm defects, and crystals with ~ 1000 ppm defects. For virgin crystals the 29 cm^{-1} feature had a peak height of 8% at 2K. With ~ 100 ppm defects the peak height was only 3%. With ~ 1000 ppm defects, the peak was unobservable above the noise level of 1%.



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Fig. 3 - FIR reflectance vs. radiation-induced defects for samples with 0, ~ 100 , and ~ 1000 ppm defects, showing the effect on the 29 cm^{-1} feature.

Analysis

A Kramers-Kronig analysis of the FIR reflectance of $(\text{TMTSF})_2\text{ClO}_4$ reveals sharp peaks in $\text{Re}(\sigma)$ centered at 7 and 29 cm^{-1} with magnitudes of ~ 1000 and ~ 7000 ($\text{ohm}^{-1}\text{cm}^{-1}$) and widths of 1 and 2 cm^{-1} respectively, depending somewhat upon the high frequency extrapolation chosen for the reflectance. Such strong, sharp modes are typical of coupled electron-molecular vibrational modes found in the IR spectra of many organic charge transfer compounds. Examples include $(\text{TMTSF})_2\text{ReO}_4$, $(\text{TMTTF})_2\text{PF}_6$, and possibly $(\text{TMTSF})_2\text{PF}_6/6/$. However, the low frequency of these modes in $(\text{TMTSF})_2\text{ClO}_4$ is unusual. The enormous oscillator strength of these modes is essentially electronic in origin [7,8]. The electron-phonon coupling in $(\text{TMTSF})_2\text{ClO}_4$ which gives rise to strongly IR-active modes is possibly a result of the dimerization [8,9] of this compound. Since an onset of $\text{Re}(\sigma)$ with increasing

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Work support Sciences, Ma Contract No.

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frequency would be expected for a superconducting pseudogap, the observed sharp peaks do not support the hypothesis of fluctuational superconductivity.

Radiation-induced defects are known to have a strong effect upon the electronic properties of $(\text{TMTSF})_2\text{ClO}_4$ and related salts. For example, a defect concentration of 100 ppm in $(\text{TMTSF})_2\text{PF}_6$ is sufficient to suppress the superconducting transition from 1K to below 20 mK, and at 1000 ppm defects, the spin density wave transition at 12K is suppressed /10/. Similar sensitivity to radiation damage might be expected for other electronic effects. It is not surprising, therefore, that defects suppress the 29 cm^{-1} feature, which is largely electronic in origin.

An experiment /1/ very similar to the magnetotransmittance experiment described here did show a magnetic field dependence for the 29 cm^{-1} feature, in contrast to our results. Several differences exist between these two experiments which may explain the different results. These include the sample temperature which was somewhat lower (1.2K to 2K compared with $T_c \sim 1\text{K}$) /1/, the rate of cooling (which has been found to have a significant effect upon the superconducting transition temperature /11/ and the appearance of a magnetic state below $\sim 3.5\text{K}$ /12/), or in the samples themselves, which come from different sources. Aside from the field effect, most other results of the two experiments are in good qualitative agreement /10/.

Conclusions

Reflectance measurements of $(\text{TMTSF})_2\text{ClO}_4$ between 4 and 40 cm^{-1} reveal peaks at 7 and 29 cm^{-1} at low temperatures. The peaks gradually disappear with increasing temperature above 20K, but are still evident up to 60K.

Radiation-induced defects suppress the 29 cm^{-1} reflectance peak. A defect concentration of 1000 ppm is sufficient to reduce the peak height by more than an order of magnitude.

Magnetotransmittance measurements of the 29 cm^{-1} feature at 2.3K and 4.2K show no magnetic field dependence.

A Kramers-Kronig analysis of the reflectance reveals strong, narrow peaks in $\text{Re}(\sigma)$ at 7 and 29 cm^{-1} . These are believed to be electron-molecular vibration coupled modes. The shape, strength and field independence of these features do not support an interpretation in terms of a superconducting pseudogap.

Acknowledgments

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